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TITLE: An Apparatus for Measuring the Bulk Modulus of Solid Propellants

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ABSTRACT: An apparatus has been developed to measure the equilibrium bulk modulus of solid propellants and other visco-elastic materials at pressures between 0 and 2500 psig. Hydrostatic pressure is applied to a test sample in the high-pressure chamber of a pressure intensifier. Measurement of the volume displaced by the low-pressure end of the double piston provides high sensitivity in the measurement of the volume change in the high-pressure chamber. The measured isothermal modulus is sufficiently accurate for use in quasi-static stress analysis of solid-propellant rockets. In addition, the adiabatic bulk modulus can be estimated from pressure-volume-temperature data. Small voids in a propellant are vividly shown by a very fast initial rise in the curve of pressure vs. volume change.

SESSION B-III-3

TITLE: Determination of the Critical Torque Inducing Buckling in a Twisted Spherical Shell Subject to Internal or External Pressure

AUTHOR: MOW and SADOWSKY
Watervliet Arsenal

ABSTRACT: The problem of determining the critical value of the torque T inducing buckling in a pressurized twisted spherical shell has been solved under assumption of local non-analytic buckling. The critical relation between the values of the torque T and pressure p has been explicitly determined.

AN APPARATUS FOR MEASURING THE BULK MODULUS OF SOLID PROPELLANTS

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INTRODUCTION

The mechanical behavior of the propellant is of considerable importance in the design of a solid-propellant rocket because the propellant must be sufficiently stiff to minimize creep during storage and yet must not be so brittle that it may crack under the pressures at which it burns. Some solid propellants are homogeneous compounds while others are composite mixtures of crystalline oxidizers and other additives in a small amount of binder. Both types of solid propellant, however, are predominantly viscoelastic in their mechanical behavior.

The basic methods for solving problems in stress analysis are well established for elastic materials. The classical theory of elasticity is limited almost entirely to situations in which the strains are small. The strains set up within an elastic material are linear functions of the stresses under all conditions of loading, provided the elastic limit is not exceeded; that is

$$\frac{\text{stress}}{\text{strain}} = \text{constant (modulus of elasticity).} \qquad (1)$$

When the strains are small, only two elastic constants are required to describe the mechanical behavior of a material that is homogeneous and isotropic. If, for example, the shear modulus (modulus of rigidity), G, and the bulk modulus, K, are determined, then Young's modulus, E, and Poisson's ratio, ν, can be calculated from the relations

$$E = \frac{9KG}{3K + G} \quad \text{and} \quad \nu = \frac{3K - 2G}{6K + 2G} \qquad (2, 3)$$

which have been given by Southwell (1) a[illegible]thers. Any of these moduli may be replaced by their correspo[illegible]g reciprocals, 1/J, 1/B, and 1/D, where J is shear compliance, B is bulk compliance (compressibility), and D is tensile compliance. The shear and bulk moduli may be regarded as the fundamental elastic constants from a physical point of view because the former measures the resistance of a material to change of form unaccompanied by change of volume and the latter measures its resistance to change of volume unaccompanied by change of form.

The stress analysis of viscoelastic materials is somewhat more complicated, not only because these materials are time-dependent, but also because they deviate measurably from the behavior predicted by the Boltzmann superposition principle (2, 3) on which the theory of linear viscoelasticity is based. For small strains, however, this deviation can be neglected for many materials and calculations can be based on linear viscoelastic behavior. In the final report of the Committee on Nomenclature of the Society of Rheology, Leaderman (4) stated that the relations between the complex moduli and compliances for dynamic viscoelastic behavior are the same as those existing between the corresponding moduli and compliances of classical elasticity theory.

Stress analysis problems involving viscoelastic materials frequently can be formulated in terms of Volterra integral equations if the moduli are known (5, 6). An alternate method sets up analogies using mechanical models consisting of suitable combinations of Hookean springs and Newtonian dashpots (7, 8). In current applications of linear viscoelastic theory, the distinction between moduli measured under adiabatic and isothermal conditions usually is ignored because this difference is in most cases negligible. Although this difference is entirely negligible in shear and the moduli seldom differ by more than a few percent in bulk, Ferry (3) has inferred on theoretical grounds that the adiabatic bulk modulus can exceed the isothermal by 20% or more for some soft polymeric solids.

At the Ballistic Research Laboratories, a study is being conducted to determine to what extent the theory of linear viscoelasticity can be applied to the stress analysis of solid propellants (9) To correlate theory with experimental results, apparatus are being devised to measure the bulk and shear moduli under various conditions. Preliminary study has indicated that the equilibrium bulk modulus is satisfactory for quasi-static problems such as the slow deformation of a propellant in storage. However, the adiabatic bulk modulus is better for approximate solutions of dynamic problems.

The apparatus described in this paper was built to measure the equilibrium bulk modulus of solid propellants and other viscoelastic materials under hydrostatic pressures of 0 to 2500 psi (gage). It was built after preliminary tests had indicated that such an apparatus was feasible (10). Very little information has been reported in the scientific literature concerning hydrostatic modulus or compliance testing in this pressure range. Bridgman (11) has worked with several viscoelastic materials, but only at very high pressures. Sweeny and Bills (12) have made a few pressure-volume measurements on solid propellants. Milloway, Surland, and Skulte (13) have recently reported that the composite propellants used in their testing are sufficiently isotropic in hydrostatic compression that bulk modulus can be calculated from uniaxial displacement measurements.

APPARATUS AND EXPERIMENTAL PROCEDURE

This apparatus is designed to determine the bulk modulus of a solid by substituting the solid for some of the liquid in the test chamber, measuring the net compressibility of the solid plus the remaining liquid, and applying differential methods to separate their compressibilities. The intensifier principle is utilized to obtain high sensitivity in measurement of the volume changes produced by variation of the hydrostatic pressure. The test sample is placed directly in the high-pressure chamber of the intensifier to minimize the volume of fluid required and therefore minimize the influence of the fluid on the test data (Figure 1). A test chamber of approximately 1 cu. in. was selected so that small propellant samples (up to 1/2 in. in diameter by 3 in. in length) can be tested effectively.

The apparatus was designed for operation at pressures from 0 to 2500 psig because this range covers the pressures that occur during the burning of most solid-propellant rockets. However, the intensifier principle could be used for much higher pressures (or larger chamber volumes) with appropriate design. The piston seals are a modification of Bridgman's (11) unsupported area seal. The slipperiness of the teflon seals permits observation of pressure-volume data at pressures close to 0 psig even though the seals are preloaded to minimize leakage at these low pressures.

In addition to the pressure intensifier, the bulk modulus tester utilizes auxiliary equipment and instrumentation including a sight-glass system, hydraulic pumps, valves and fittings, a dial pressure gage, a pressure transducer, a strain indicator or recorder, a thermocouple, a microvolt amplifier, and a strip-chart recorder. A photograph of the system is shown in Figure 2.

The total volume of the test chamber and its connecting passageways was obtained by measurement and calculation. The relationship between the volume change in the chamber and the sight-glass reading also was calculated. The pressure transducer was calibrated in conjunction with the strain-indicator and a standard dead-weight tester. The chromel-alumel thermocouple was set up to measure the temperature change within the chamber. The temperature scale of the recorder chart was established from thermocouple data sheets since they provided sufficient accuracy for this test.

During the initial setup of the apparatus, a vacuum pump is used to evacuate each chamber as it is filled with hydraulic fluid.

Hercoflex 600 hydraulic fluid has been used with solid propellants at the BRL. Hercolube A or Dow-Corning DC-550 probably would be equally satisfactory. If necessary, the test sample may be given an impermeable coating to prevent penetration of the fluid into the pores or to prevent a possible chemical reaction. When a sample is prepared for testing, the test chamber is filled to overflowing before installing the closure so that no air will be entrapped. This precaution is essential because a major problem in an apparatus of this sort is the complete elimination of air in the test chamber. For critical tests, much of the air dissolved in the working fluid can be removed by boiling under vacuum prior to filling the system.

The apparatus was calibrated by measuring the pressure and volume changes for steel samples of different sizes. With the sample in the high-pressure chamber, pressure is applied to the low-pressure chamber by a hand pump. The pressure is intensified as it is transmitted to the smaller chamber by the double-faced piston, and as the piston moves, the excess fluid enters the sight glass from the middle chamber. Measurement of the volume displaced by the low-pressure end of the double piston provides a very sensitive measurement of the volume change in the high-pressure chamber. During isothermal testing, an interval of approximately 10 minutes is allowed prior to recording the data for each pressure so that temperature equilibrium will be reached. The second pump is used to return the piston to its starting position after each test is completed.

To obtain adiabatic data, the system is quickly pressurized from 0 psig to a desired pressure and the pressure-volume-temperature data is recorded immediately. The pressure is then dropped to 0 psig and the system is allowed to return to equilibrium temperature. The cycle of operation is repeated for each additional pressure that is needed.

ANALYSIS AND DISCUSSION

As previously stated, this apparatus was designed to measure the equilibrium bulk modulus of solid propellants and other viscoelastic materials. The bulk modulus is the ratio of the volumetric stress (hydrostatic pressure) to the volumetric strain (volume change per unit volume),

$$K = - \frac{\Delta P}{\Delta V/V} . \tag{4}$$

The negative sign is introduced because hydrostatic tension is normally considered positive and the application of a hydrostatic pressure produces a decrease in volume. In the direct measurement of the bulk modulus of a solid by immersion in a liquid, differencing techniques are applied to correct for the compressibility of the fluid and for the distortion of the test chamber. The initial volume of the chamber is equal to the sum of the sample and fluid volumes,

$$V_c = V_s + V_f \,. \tag{5}$$

When pressure is applied by movement of the piston, the new chamber volume is

$$V_c + \Delta V_c = V_s + \Delta V_s + V_f + \Delta V_f = V_c + C'\Delta P - \Delta s \pi r^2 \,, \tag{6}$$

where C' is a constant that accounts for the pressure effects on the chamber itself (expansion of chamber, pressure gage, and connecting passageways; compression of seals), Δs is piston travel, and r is the radius of the piston. Second order effects are small in the pressure range under consideration, and their effect on the data are minimized by the differencing technique described herein. The volume change per unit pressure is

$$\frac{\Delta V_c}{\Delta P} = \frac{\Delta V_s}{\Delta P} + \frac{\Delta V_f}{\Delta P} = -\frac{C''\Delta h}{\Delta P} + C' \,, \tag{7}$$

where Δh is the change in the height of the sight glass column and C" accounts for the magnification of the piston motion by the sight glass system.

Combining Eq. (4) and Eq. (7), the bulk modulus of a test sample may be written

$$K_s = -\frac{V_s}{\Delta V_s/\Delta P} = \frac{V_s}{(C''\Delta h/\Delta P) - (V_f/K_f) - C'} \,. \tag{8}$$

The bulk modulus of the sample is determined from the measurements of the sight glass reading, Δh, and the applied pressure, ΔP, after the other items have been established. The initial volume of the chamber, V_c, is determined by measurement and calculation. Measurement of the initial sample volume, V_s, then yields the initial volume of fluid, V_f. The sight glass magnification constant, C", is calculated from the sight glass and piston diameters. The bulk modulus of the fluid, K_f, and the chamber expansion constant, C', are determined during calibration of the apparatus.

The apparatus is calibrated by using various sizes of test samples with a known bulk modulus. The reference samples that were used were made from cold-rolled steel, which has a bulk modulus of approximately 23.1×10^6 psi (14), nearly 100 times that of the transmitting fluid. From Eq. (8), it is seen that the equation

$$\frac{C''\Delta h}{\Delta P} - \frac{V_s}{K_s} = \frac{V_f}{K_f} + C' \tag{9}$$

is an equation of the linear form y = mx + b. On a plot of V_f vs $\Delta V/\Delta P$, the above equation represents a straight line with a slope of $1/K_f$ and an intercept on the $\Delta V/\Delta P$ axis of C'. The measurement of Δh

and ΔP for two different fluid-sample combinations is sufficient to determine the slope and the intercept. In practice, seven combinations were used and the method of least squares was applied to obtain the best average slope and intercept.

During the tests of samples of various materials, the minimum number of observations per test was six and the method of least squares was again applied to obtain the best average slope $\Delta h/\Delta P$. The bulk modulus was then calculated from Eq. (8). Equilibrium bulk moduli of several viscoelastic materials and the transmitting fluid are tabulated in Table I for two pressure ranges, 0-2500 psig and 500-2500 psig.

TABLE I. EQUILIBRIUM BULK MODULI, IN PSI, OF SEVERAL VISCOELASTIC MATERIALS AT 77 ± 1°F

Material	Pressure Range, psi (gage) 0 - 2500	500 - 2500
Hercoflex 600 Fluid	249,000	252,000
Polystyrene (commercial rod)	472,000	476,000
Teflon (commercial rod)	363,000	367,000
Polyurethane (pluracol base)	258,000	267,000
Propellant No. 1 (cast double base)	432,000	438,000
Propellant No. 2 (composite double base)	583,000	621,000
Propellant No. 3 (composite)	834,000	882,000

The bulk modulus of each material is quite linear between pressures of 0 and 2500 psig when there are no voids. However, porous materials show large differences between their average moduli over the two ranges tabulated here because the voids undergo considerable compression at low pressures. With soft composite propellants, the effect of voids on the compressibility can be ignored above approximately 100 psig. The tabulated moduli for the propellants are taken from the second compression cycle for each material because the initial cycles were very non-linear while the voids were being compacted. The stress-strain relationship observed with teflon, a fairly dense material, is illustrated in Figure 3. In contrast, Figure 4 shows a composite double-base propellant with an initial porosity of approximately 0.33%. The propellant is compacted on the first test cycle, resulting in a porosity of less than 0.05% on the second run, which was made several hours later.

As indicated in the preceding paragraph, the porosity of a soft viscoelastic material can be determined with this apparatus. The intercept of the observed stress-strain curve with the strain-axis at zero applied stress provides a measure of the strain resulting from closure of voids. The porosity of the material is the ratio of this strain to the initial sample volume. Porosities of 0.01% can be measured by this procedure. The effect of voids on the compressibility data can be observed closely at low pressures because the slippery teflon piston seals permit the piston to creep in the cylinder at applied loads considerably below the preload on the seals.

Actually, the volumetric stress-strain ratio for a material is not linear because its resistance to compression increases as its volume is reduced. Bridgman (11) and others have verified through extensive testing that, except for a few rare cases, the compressibility decreases with increasing pressure, as would be expected. This can be observed on the curves of Figure 3, where the data points are connected by a smooth curve, and Figure 4, where the points are represented by straight lines. Further analysis of the experimental data indicates that the tangent bulk modulus increases linearly with pressure in the manner predicted by the Tait equation of state for liquids (15),

$$- \frac{dP}{dV} = mP + b \, , \tag{10}$$

where m is a constant, b is a function of temperature only, and $-dP/dV = K/V$ [Eq. (4)]. The constants are easily established by graphical or analytical methods. Isothermal data from tests of the fluid, a teflon sample, and a propellant sample indicate that the Tait equation provides an accurate fit to the experimental data after the voids, if any, are closed. This equation should also be useful in correlating isothermal and adiabatic data.

The precision of measurement of this apparatus is such that changes of .00001 cu. in. in the volume of the chamber are readily detected and changes to .01 cu. in. can be measured with the present sight glass. These measurements compare with the initial chamber volume of .942 cu. in. and a maximum sample size of .57 cu. in. Larger volume changes could be measured with a glass of larger diameter, but at a sacrifice in precision. The use of two sight glasses in tandem would permit testing of very porous materials, using the larger glass for porosity data and then switching to the precision glass for modulus data.

The accuracy of the bulk moduli measured with this apparatus has not been established because a search of the literature has not revealed a suitable reference standard for this low pressure range. Based on a 95% confidence level, the bulk modulus of a test sample should be repeatable within 2%. However, this does not account for the deviations during calibration and systematic errors in measuring the dimensions of the sight glass and test chamber. There also is the problem of measuring the initial volumes of test samples having irregular shapes. A sample of an unknown aluminum alloy, which should have a bulk modulus close to 10×10^6 psi (about 30 times that of the transmitting fluid), was tested while running the calibration tests with the steel samples. Its modulus appeared to be between 9 and 12×10^6 psi. This implies accuracies within ±2% for viscoelastic materials, which is questionable.

The hydraulic fluid and viscoelastic samples are very sensitive to temperature changes. When a sample of maximum size (61% of chamber volume) is under test, the thermal expansion of the fluid (39%) for a temperature rise of 1 $^{\circ}$F is as great as the volume reduction of the aluminum sample at 2500 psig. The thermal expansion of the test sample may increase the total expansion by another 50%. Therefore, extremely close control over temperature must be exercised.

Although this apparatus was designed specifically for equilibrium (isothermal) testing, the measurement of temperature change inside the test chamber in conjunction with the P-V data permits determination of the adiabatic bulk modulus of the transmitting fluid and estimation of the adiabatic bulk modulus of the test sample. The modulus of the fluid is separated from the equivalent modulus correction for the apparatus through differential analysis of the calibration test data, as has been done for the isothermal testing. This same technique is then applied to estimate the adiabatic modulus of the test sample. Since these results are quite inaccurate, adiabatic testing has been limited to exploratory runs. A larger apparatus, in which a thermocouple is imbedded in the sample and the fluid volume is minimized, would be more desirable for adiabatic measurements.

A major problem in this apparatus was complete elimination of air in the pressure chamber. A preliminary apparatus (10) assembled from standard high-pressure laboratory equipment was only partially successful because of this defect. The new apparatus was designed to permit evacuation of the test chamber, and the other chambers, from one side while filling from the other. Each individual test was set up with great care to insure the reliability of the test data.

This compressibility apparatus is relatively safe since it avoids the danger associated with the large kinetic energies of gas-filled pressure bombs. If any sudden surge of pressure should occur, it would cause the pressure transducer to fail without danger of flying metal fragments. However, with minor changes, the system could be set up for remote operation.

SUMMARY AND CONCLUSIONS

This apparatus provides a measure of the equilibrium bulk modulus and compressibility of solid propellants and other viscoelastic materials at pressures between 0 and 2500 psig. The test sample is placed in the high-pressure chamber of a pressure intensifier. As hydrostatic pressure is applied, measurement of the volume displaced by the low-pressure end of the double piston provides high sensitivity in the measurement of the volume reduction in the high-pressure chamber. The measured isothermal modulus is sufficiently accurate for use in the quasi-static stress analysis of solid-propellant rockets. In addition, the adiabatic bulk modulus can be estimated from pressure-volume-temperature data. Porosities as small as 0.01% also can be measured for soft viscoelastic materials and the rapid initial rise in the pressure-volume curve shows the effect of voids on the bulk modulus. Test results indicate that porous materials do not fully recover from the compacting effect of hydrostatic pressure, thus indicating that such a procedure might be used to increase the density of porous propellants.

This apparatus is quite satisfactory for the measurement of the bulk modulus of small samples (up to 1/2 in. in diameter by 3 in. in length) and it is especially applicable to the testing and screening of the small samples normally available with newly-synthesized experimental propellants. The principle weakness of this apparatus is the masking of the properties of the test sample by the transmitting fluid, which fills at least 39% of the test chamber, is 1 to 3 times as compressible as the sample, and has a relatively high coefficient of thermal expansion. However, the apparatus is safe and its operation is fairly rapid because it employs a continuous reading method. Where more material is available for test samples, a larger test chamber could be utilized. To provide for greater accuracy in both isothermal and adiabatic testing, the volume of fluid should be minimized and a thermocouple should be imbedded in the test sample.

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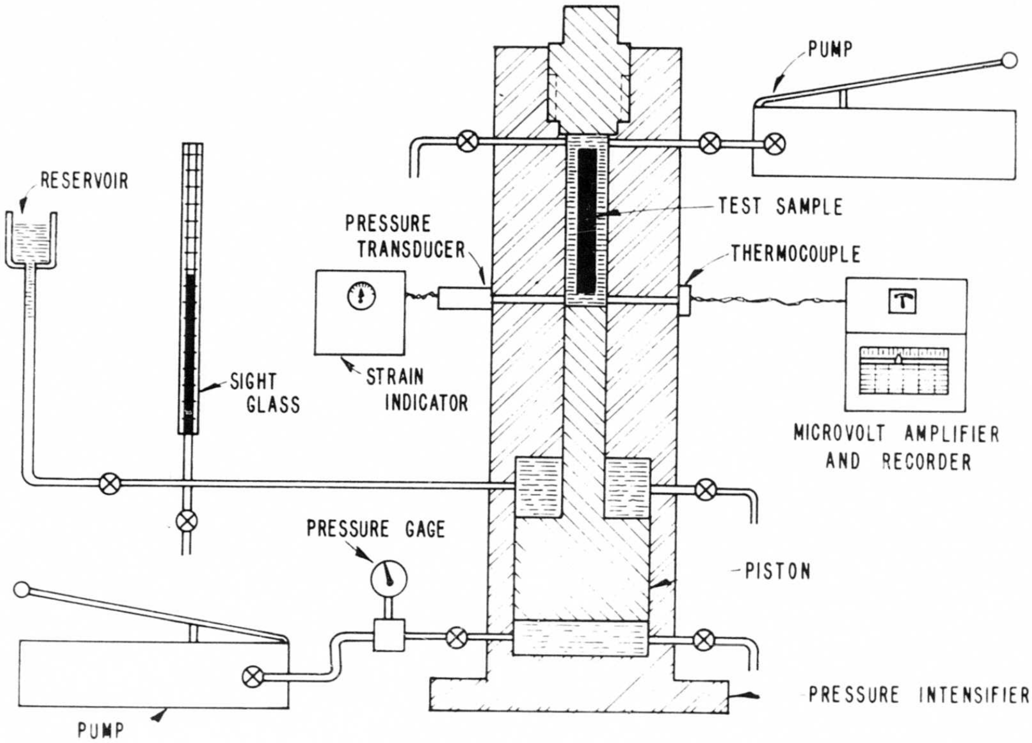

Figure 1. Schematic Drawing of Bulk Modulus Apparatus

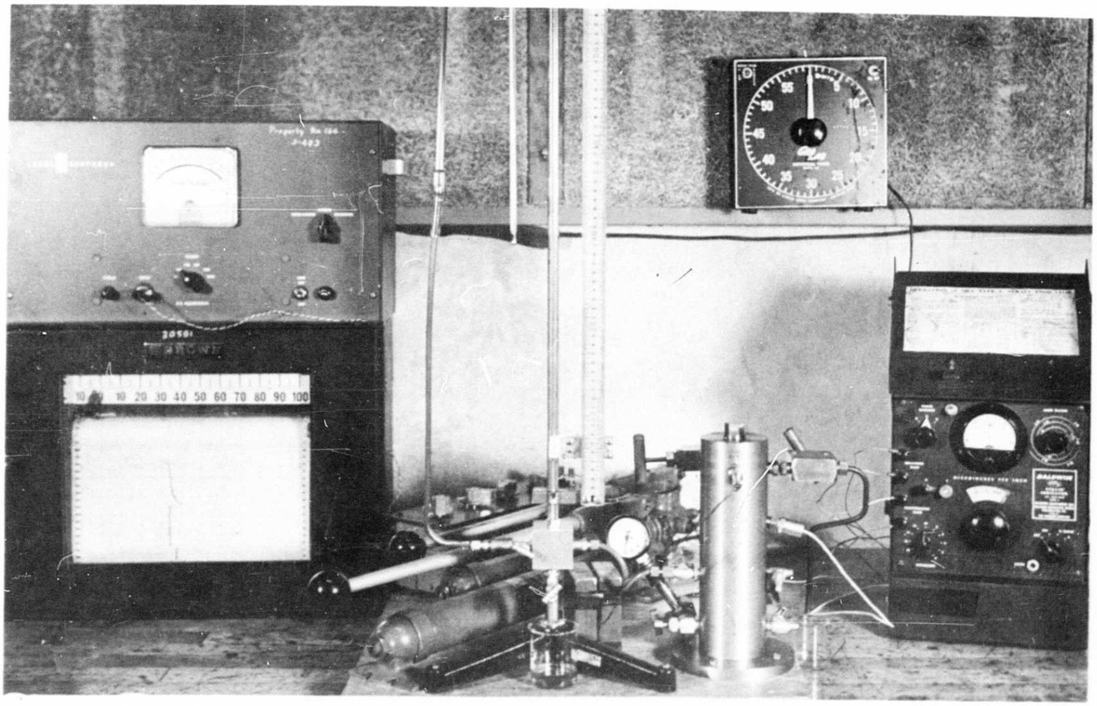

Figure 2. Bulk Modulus Apparatus

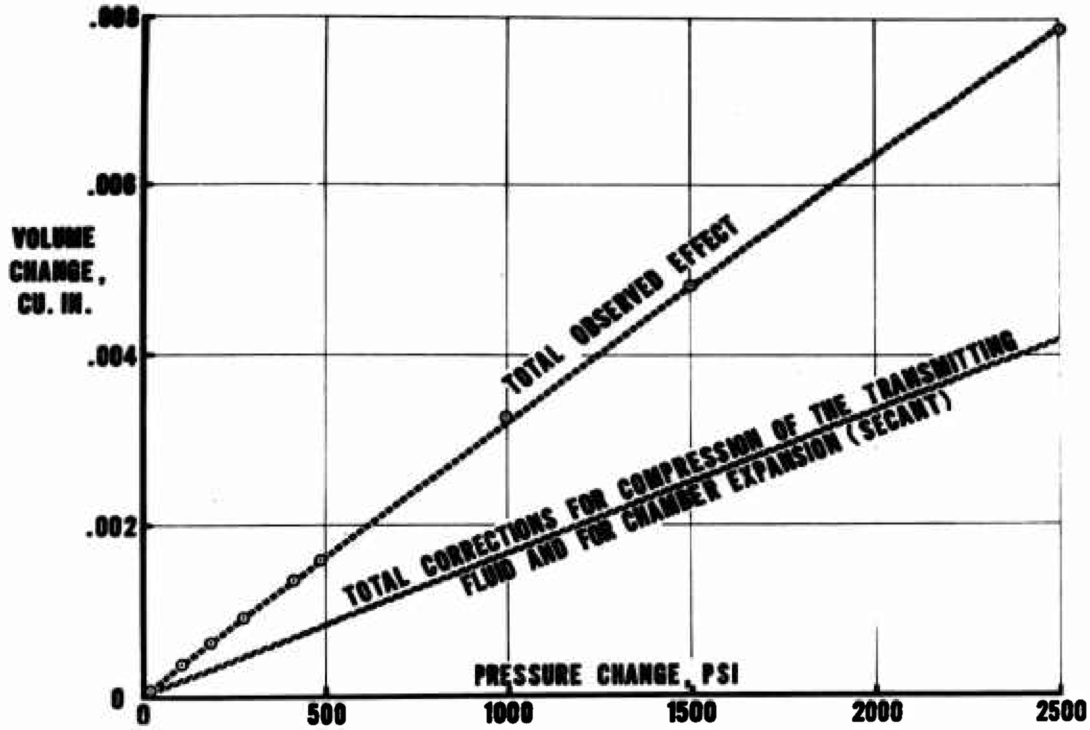

Figure 3. Pressure-Volume Curve for a Teflon Sample

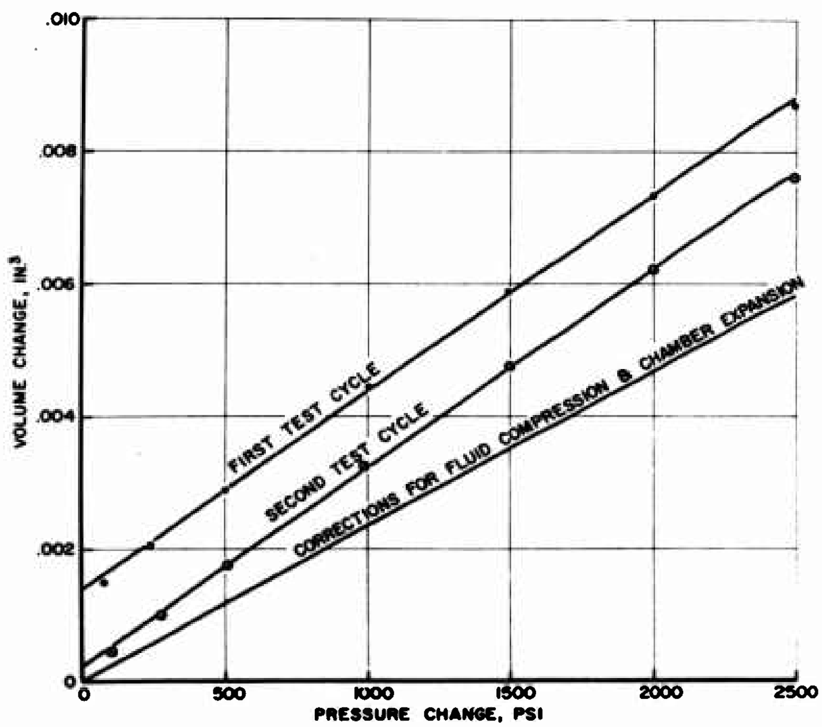

Figure 4. Pressure-Volume Curves of Propellant of 1/3% Initial Porosity